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Virtues of Composite Structures in Electrode Modification. Preparation and Properties of Poly(aniline)/Nafion Composite Films.

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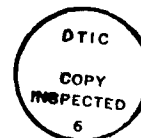
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Abstract - Poly(aniline) (PA) is electropolymerized within thin films of precast Nafion on gold or glassy carbon electrodes. The quartz crystal microbalance (QCM) is used to aid in identification of the ionic species which undergo transport during switching of the PA between its insulating and conducting forms. The QCM frequency changes observed in solutions containing various cationic species suggest that cation transport is dominant for these composite structures. In acidic solution, a consequence of the high transport number for the proton in the composite films is shown to be an enhanced switching rate relative to the simple (non-composite) PA film. The composite PA films appear to be less resistive and therefore more electrochemically well behaved over a wider pH range than the simple PA films.



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Introduction

Composite structures offer opportunities for enhancing the functions of synthetic microstructures on electrodes in that they provide a means to construct heterogeneous materials which have more desirable properties than those of the individual components. Nafion provides a good example of the unique properties available from such heterogeneous materials. Films of Nafion (whether cast or in the commercially available membrane form) exhibit some degree of phase segregation (1) which leads to unusual stability towards dissolution while providing a sufficiently hydrophilic environment to allow for solvent and ion transport required for electrochemical reactions within the film (2). These properties of the composite film have been used to advantage in electrocatalytic applications (3). Other examples of the preparation of heterogeneous materials on electrodes, achieved with composite structures, include a) the polymerization of pyrrole in a poly(vinylchloride) matrix (4), in Nafion (5,6), in Nafion-impregnated Gore-tex (6), in clay films (5), and in poly(vinylalcohol) films (7), b) electrochemical preparation of tetrathiafulvalinium bromide structures within Nafion films (8), c) fabrication of porous aluminum oxide layers on electrodes and their use to study electron transport in monolayer and polymer systems (9), and d) a recent study of the influence of electropolymerization of PA within precast films of poly(methylmethacrylate) and poly(acrylic acid) (10). A recent contribution by Wnek discusses the advantages of composite formation for enhancing the mechanical properties of conducting polymers prepared by chemical (as opposed to electrochemical) methods (11).

A particular area in which the enhancement in materials properties of such structures might be especially applicable is in efforts to manipulate the electrochemical responses of conducting polymers or conducting salts (4-8,10). These materials are somewhat unique in that they may be facilely switched between their insulating and conducting states by oxidation or reduction. The redox process is accompanied by ion transport in order to compensate the creation of charged sites within the polymer matrix, and this transport of ionic species through the film often seems to represent the kinetic step which controls the overall switching rate (12). Thus, in order to rationally manipulate the electrochemical behavior of conducting polymers, one must first develop methods to identify the species which are transported during the redox

event, and then design a strategy through which the identities of these species may be changed and/or their transport rates increased.

It has recently been shown that the quartz crystal microbalance provides unique information on the identities of the species undergoing transport during redox events in polymer films on electrodes (13,14). The technique allows simultaneous measurement of the mass changes and electrochemical parameters in experiments with thin films on electrodes. The advantages and limitations of the technique for such measurements have been briefly addressed (13,14). The method has allowed quantitative measurements of the extent of oxidation of the polymer during switching, and, in measurements especially pertinent to the topic at hand, has revealed the extent of anion and proton transport in PA (14). These last measurements demonstrated that the fraction of charge compensation which occurs via proton (as opposed to anion) transport increases as the pH of the solution is lowered. As will be seen below, decreasing the pH also increases the switching rate for the insulator-to-conductor transition in poly(aniline). This is probably due to a combination of decreasing electronic resistance of the film at lower pH (10,14,15), as well as an increase in the fraction of the ionic charge compensation which occurs by proton transport. In the present study, a composite Nafion/PA film is shown to exhibit enhanced switching rates relative to the simple (non-composite) PA film. Also, the apparent redox potential for the PA insulator-to-conductor transition is shown to appear at a different value for the composite film. These observations are interpreted in terms of a high transport number for cationic species in the composite films, which results from the Donnan exclusion of mobile anions from the film interior.

Experimental Section

Reagent grade chemicals were used as received. Reagent grade aniline was distilled under reduced pressure to give a colorless liquid prior to use. Solutions were made with deionized water from a Millipore purification system.

The experimental apparatus for the electrochemical and QCM measurements has been described (13,14,16). It is useful to recall that the mass sensitivity for a 5 MHz AT-cut QCM crystal of the type used in this study is $56.6 \text{ Hz/microgram/cm}^2$, i.e. that a mass change on the QCM gold electrode of 1 microgram/cm^2 will cause a change in the resonant frequency of the QCM crystal of 56.6 Hz. Gold films of thickness 300 nm were deposited onto the quartz crystals using an Edwards E306A vacuum coating system, and were used

throughout as the working electrode material on the QCM crystals. All potentials are quoted versus a sodium chloride saturated calomel electrode (SSCE).

Films of 1000 equivalent weight Nafion (Solution Technologies, Mendenhall, Pennsylvania) were cast by syringing aliquots (typically 2 microliters) of a 5.0% solution onto the gold electrode surface and allowing the films to dry very slowly in an atmosphere of saturated isopropanol. This procedure was found to greatly increase the uniformity of the films, as judged by optical microscopy. Rapid evaporation is known to give distinctly non-uniform films (17). Care was taken to cast films of reproducibly uniform thickness because film uniformity is a critical issue in studies using the QCM for quantitative mass measurements due to the dependence of the QCM mass sensitivity on the radial position from the center of the QCM electrode (18).

The PA was electropolymerized on the bare gold QCM electrodes by potential cycling in 1.0 M H_2SO_4 and 0.1 M aniline, as described previously (14). Electropolymerization within the Nafion matrix was effected by the same procedure using a gold QCM electrode which had been derivatized by application of a thin Nafion film as described above.

Results and Discussion

Film Growth and Cycling Behavior. In a previous contribution, the use of the QCM to monitor growth of thin films of PA during electropolymerization was described (14). The technique was shown to offer sufficient sensitivity to observe the deposition of films of the polymer as thin as 1.5 nm. For reference, this amount of deposited mass corresponds to a frequency change of 10 Hz. In addition, the fluxes of ionic species were monitored during the electrochemically induced transition between the insulating and conducting states of PA. A detailed analysis of these fluxes as a function of the pH of the solution revealed that both anions and protons are involved in the charge compensation (14).

Figure 1 shows the result of a similar experiment in which PA was electropolymerized within a precast Nafion matrix on the QCM gold electrode. The data in the figure represent a typical cycle recorded during the electropolymerization of the PA. The features in the cyclic voltammogram (CV) caused by the redox process for the insulator-to-conductor transition of the film are evident as a relatively sharp anodic wave at 0.15 V and a relatively broad cathodic wave at 0.08 V. These features are evident in this scan because

the CV was recorded after considerable growth had already taken place. At more positive potentials, the oxidation of aniline monomer is observed as an irreversible anodic process at ca. 0.7 V. The shapes and potentials of the features in the CV of a film of PA which is being electropolymerized within a Nafion matrix are essentially identical to those observed on a bare gold electrode (14).

The QCM response for the growth cycle is also shown in Figure 1 as Curve B. The frequency of the resonator is seen to remain nearly constant throughout the cycle, with only a very small (ca. 1 Hz) decrease observed at the positive end of the scan. This is in marked contrast to the behavior observed for growth of simple PA films (14). In the latter case, the process responsible for the anodic peak at 0.15 V initiates a significant frequency decrease (the magnitude of which depends linearly on the film thickness at a given pH) which continues as the potential is scanned more positively. This is caused by anion insertion to compensate for the creation of positively charged sites within the film. One also observes a net frequency decrease of ca. 10 Hz (caused by deposition of new film material) during the cyclic voltammetric scan for electropolymerization of PA onto bare gold electrodes under the same conditions as those in Figure 1.

Figure 2 illustrates the behavior of PA films which have been grown to such an extent that the thickness of the conducting polymer layer exceeds that of the Nafion matrix (a fact which was verified by optical microscopic observation of fibrils of the conducting polymer which protruded from the surface of the Nafion/PA composite film). In this case, the oxidation process leads to a frequency decrease due to anion insertion just as for the simple PA film (14). However, the magnitude of this decrease is much smaller than would be observed for a simple film of equivalent thickness. For example, a simple PA film with a peak current of 0.8 mA (the same as that of the composite film in Figure 2) would exhibit a frequency decrease of 160 Hz. The composite film shows a decrease of only 40 Hz.

In contrasting the behavior of the simple PA film with that of the composite film one needs to account for two obvious differences. The first is that, as shown in Figure 1, the growth of PA within the Nafion matrix appears to proceed with no apparent mass gain (or loss), while that of the simple film proceeds with large, measurable increases in electrode mass (14). Since there are several phenomena which could occur during the electropolymerization

process, there are also several scenarios which could produce this type of behavior. One is that the anilinium cations which are electropolymerized existed within the Nafion matrix prior to polymerization. Mass and charge balance considerations discussed below argue that this case will lead to experimentally insignificant frequency changes. In addition, depending on changes in the water activity within the film caused by the film growth, solvent may flow in either direction across the film/solution interface, adding considerably to the complexity of the situation. The second important difference between the simple and composite films is that, in the composite film, the redox process responsible for the insulator-to-conductor transition appears to occur with no mass gain, while that for the simple films is accompanied by a large frequency decrease due to anion insertion for charge compensation. We propose that this behavior results from differences in the charge compensation processes for the two films. The simple films are known to exhibit both anion and proton transport with transport numbers approaching 0.5 for each, while it will be shown below that the composite films appear to have a higher transport number for the proton during switching. In the next section we demonstrate enhanced switching rates for the composite films relative to the simple films, a kinetic consequence which can be attributed to the proposed differences in charge compensation mechanisms.

It is important at this point to address the issue of the influence of the mechanical properties of the Nafion films on the QCM mass measurements. As has been previously discussed (13,14), changes in the viscoelastic properties of the film can influence the QCM frequency, either increasing or decreasing the mass sensitivity depending on the size and direction of change of the film viscosity and shear modulus. However, based on the following reasoning, it seems clear that lack of observable frequency changes for the film growth and charging processes described above is not the result of non-rigid behavior for the Nafion composite. If the films were behaving viscoelastically in such a way that the observed frequency changes for these processes were near to zero, this would imply nearly complete attenuation of the QCM acoustic shear wave within the composite. However, the data in Figure 2 show that shear wave attenuation within the Nafion matrix is not significant because when the PA is grown sufficiently thick to extend beyond the Nafion film, one begins to observe frequency decreases during the film growth and charging processes. In fact, direct comparison of the incremental charge for that amount of the PA

which appears to have grown past the Nafion matrix with the frequency decrease observed during oxidation of this material shows that it behaves in exactly the same way as does the simple film, i.e. the mass to charge ratio is the same for this material and the simple film. This is very good evidence that the mass sensitivity is not influenced by the presence of the Nafion matrix, because if the shear wave were being damped as it travelled through this matrix, then the sensitivity for detecting mass changes in the outermost regions of the composite film would be significantly decreased. This does not appear to be the case. Thus, the lack of significant frequency changes during growth and charging of PA within the Nafion matrix leads to the conclusion that very little mass change accompanies these processes. An explanation of this observation requires a detailed examination of the polymerization and switching reactions.

Assuming head to tail coupling of the monomers in the polymer (10,14,15) and neglecting end group effects, one can write the polymerization stoichiometry as shown below. The polymerization of one mole of anilinium

(Insert Scheme 1)

cations is seen to produce $(3p+2q)$ moles of protons within the Nafion matrix, where p is the fraction of deprotonated nitrogens in the reduced form of PA (i.e. $p+q=1$). Due to the constant number of immobile anionic sites within the Nafion ionomer film, the number of cations must also remain constant. Thus, since the films are permselective (19), electroneutrality requires that q moles of cationic polymer sites and p moles of protons provide compensation for the fixed anionic sites of the Nafion component. Since the polymerization produces protons, it seems reasonable to assume that the pH equilibrium across the film/solution interface will be perturbed, resulting primarily in the expulsion of protons for charge compensation, however, expulsion of monomeric anilinium cations which have not yet been polymerized is also possible. If proton expulsion were to occur exclusively, then $2p+2q$ moles of protons would be expelled for each mole of anilinium cations which were polymerized. An estimate of p can be made based on the previous determination of the degree of protonation of the PA film as a function of acid concentration (14). This estimate requires an assumption of the effective pH within the Nafion film. Since this value is not readily available, we make the grossly simplifying

assumption that the acid concentration within the matrix is equal to 2.0 M, the effective concentration of sulfonate sites for 1000 equivalent weight Nafion (calculated assuming a film density of 2gm/cm^3). Under these conditions, p will be approximately 0.5. The total number of moles of anilinium units which have been polymerized within the Nafion matrix may be estimated from the electrochemical charge consumed during the anodic scan in Figure 1 based on previous results showing the dependence of this charge on the number of moles of aniline units in the PA polymer (14). This calculation gives $\Gamma = 5 \times 10^{-9}$ mole/ cm^2 of aniline units in the film. Thus, the polymerization proceeds with conversion of roughly 5×10^{-9} mole/ cm^2 of anilinium cations from monomers to polymer, production of $(3p+2q)\Gamma$ or 12.5×10^{-9} mole/ cm^2 of protons, and net deprotonation of 2.5×10^{-9} mole/ cm^2 of the aniline units after polymerization. Assuming permselectivity, electroneutrality requires expulsion of $(2p+2q)\Gamma$ or 10^{-8} mole/ cm^2 of cations. If these were all anilinium cations, then a frequency increase of 52 Hz would have been observed for the polymerization of the film. Exclusive expulsion of (unhydrated) protons would give a frequency increase of only 0.56 Hz, while our measurements indicate a mass decrease of slightly larger magnitude. Thus, considering the additional uncertainty due to possible solvent transport into or out of the film, we are not able to unambiguously determine the details of the mass balance for the polymerization reaction within the film. However, the above consideration of the polymerization stoichiometry indicates that it is not unreasonable to suppose that an extremely small net mass change results from polymerization of material which had previously existed within the Nafion matrix with concurrent proton expulsion and little apparent change in the solvent content of the film. That undetectably small frequency changes are observed during the switching process in the early part of the scan in Figure 1 also argues, but does not unambiguously demonstrate, that proton transport with little change in solvent content is occurring.

The ambiguity caused by the possible concurrent transport of proton and anilinium monomer during switching can be removed by examining the films in solutions containing only a single cationic species in the supporting electrolyte (in this case 1.0 M H_2SO_4). The CV/QCM experiments were done after the composite films had spent sufficient time in the acid solutions to ensure that any anilinium cations contained in the film from the polymerization solution had escaped. Thus, protons provide the only mobile cation in these

films. Scans over the range -0.3 to 0.5 V were similar to that shown in Figure 1 in that the frequency was essentially constant with potential. There are at least two possible explanations for this behavior. One is that the transport number of the cations is not close to 1 as expected, but rather that mixed cation and anion transport occurs in such a way as to result in a very small net mass change. Another is that the transport number of the proton is close to 1, and that the expulsion of protons occurs with little change in the solvent content of the composite film, thus leading to immeasurably small mass changes due to the small mass of the proton.

In an attempt to unambiguously demonstrate the presence of cation transport in these composite films, we examined their behavior in supporting electrolytes containing both CsCl and HCl (small concentrations of acid are necessary because the PA electrochemical response degrades significantly at higher pH values). Figure 3 shows results typical for such experiments. The two salient features in the figure are the **increase** in frequency during oxidation and the negative shift of the apparent redox potential for the conductor-to-insulator transition. The shift is probably due to a Donnan potential which exists across the film/solution interface caused by differences in the relative concentrations of Cs^+ and H^+ in the solution and in the film. Such effects have been recently discussed by Anson and coworkers (20). A complete description of these shifts is complicated both by the presence of protonation equilibria which are coupled to the redox process and by the presence of two cationic species in the supporting electrolyte and the corresponding competition between them for incorporation into the film. A quantitative assessment of the contributions of each of these processes to the observed shifts was not attempted in this work.

In this medium, the oxidation of the polymer clearly produces a frequency **increase** (mass decrease) which we attribute to cation expulsion. Integration of the charge in the figure reveals that 1.8×10^{-9} mole/cm² of electrons are removed from the film, requiring the expulsion of an equal number of cations. If these were all Cs^+ ions, then the frequency should have increased by 14 Hz. The observed increase is approximately 4 Hz, indicating mixed cation and anion transport and/or mixed cesium ion and proton transport and/or solvent influx concurrent with the cation expulsion. Again, the situation is such that ambiguity remains in the quantitative determination of the species which undergo transport during the redox event. However, the data in Figures 1 and 3

strongly suggest that the cationic species within the film do indeed participate in the charge compensation process. To the extent that cation expulsion dominates the charge compensation process for such films, they appear to behave quite similarly to the recently reported self-doped conducting polymers prepared by Wudl and coworkers (21).

The cyclic voltammetry of the simple and composite films was also studied at a variety of pH values. Figure 4 shows a rather striking result which illustrates an additional advantage of the composite films over the simple films. Curve A shows the CV for the simple film at a pH of 2. The anodic portion is severely distorted, presumably due to ohmic drop across the polymer layer. This is caused by the relatively low conductivity of PA at this pH which in turn results from deprotonation of the conductive form (14,15,22). In contrast, curve B shows the behavior of the composite film under the same conditions. There is no evident distortion from ohmic drop effects. Rather the CV strongly resembles the CV's observed at pH values near zero (14). We propose that this effect results from the low pH which exists within the film, in spite of the relatively higher pH in the solution. The low pH within the film is due to the presence of the immobile anionic sites of the Nafion matrix material which require that the total number of cations within the film remain constant. Since there are no other exchangeable cations in the solution which can displace the protons in the film, the proton concentration within the film remains constant despite the changing pH of the external solution. The constant, low value of the pH within the composite film leads to a more well behaved electrochemical response than that of the simple PA film at similar pH values.

Switching Rates. Chronocoulometry was used to compare the switching rates for the simple and composite PA films in acidic solutions of various pH values. Figure 5 shows data from two experiments which typify the results of such studies. It is important to note that the two films which were compared at different pH values were prepared by electropolymerization to have the same number of aniline units, so that they would consume the same electrochemical charge when stepped over a given potential range. Several pairs of films which had been prepared in this way were examined. The experiment consisted of stepping the potential from -0.2 to 0.5 V and sampling the current as a function of time after the step. The current was then digitally integrated and

plotted versus the square root of time. While this procedure does not give a true measure of the total charge due to the passage of significant amounts of charge prior to the initial sampling event, it does allow for qualitative comparison of the rate of charge consumption of these films.

The plots show clearly that the amount of charge passed after the step is not a linear function of $t^{1/2}$. Diaz et al. have also recently published an example of non-linear Anson plots for poly(aniline) (10). That these plots are not linear is not too surprising because the supporting electrolyte concentration within the film is almost certainly not larger than that of the redox sites in the film by an amount sufficient to obviate electromigration as a contributor to the magnitude of the observed currents. In addition, it has been pointed out (10) that the details of the chemical and morphological changes consequent to the conductor-to-insulator transition may influence the rate of charge propagation through such films. Finally, these films are thin enough that they may be exhibiting thin-layer behavior under these conditions. Given these considerations, it is likely that many phenomena contribute to the observation of non-linear Anson plots for such systems. The lack of linearity in these plots does not, however, invalidate their use as qualitative indicators of the rate of charge propagation in the films, especially for comparative purposes. Thus, we use the total amount of charge consumed by the films 100 milliseconds after the potential step as a qualitative indicator of the relative rate of charge propagation. This point corresponds to the end of the plots in the figure. The top curve in both plots is the Anson plot for the composite film, while the lower curve is that of the simple film. The top pair of curves were collected at pH 4 and the bottom pair at pH 3. After several seconds, the two curves in each plot converge, as required for films of equal charge capacity.

It is clear from these data that the composite films exhibit faster charging rates than do the simple films, with the effect being more pronounced at higher pH values. We propose that this is due to a relatively larger contribution to the charge transport process by proton expulsion than by anion insertion for the composite films, thereby allowing the composite films to take advantage of the larger mobility of the proton as compared to other ionic species. In addition to this effect, there is probably some contribution to the enhancement caused by the higher conductivity of the PA in the composite film due to the lower internal pH. At lower pH values (pH less than 1) the two

types of films behave essentially identically with respect to their charging rates.

That the charging rate for the composite films is higher because of a larger fraction of charge compensation by proton transport requires that the proton have a significantly higher mobility in the composite film than that of the anionic species in the simple film. Unfortunately, the proton mobility in a Nafion/PA composite film is not available. It is known that the proton has a relatively large diffusion coefficient in Nafion membranes (23). The value ranges between $1.66-0.5 \times 10^{-6} \text{ cm}^2/\text{s}$ (depending on the electrolyte concentration), or between 50 and 200 times smaller than its value in aqueous solution. The value of the diffusion coefficient of bisulfate ion in PA films may be inferred from the data of Diaz et al. (10) and Oyama et al. (24) to be on the order of $1-2 \times 10^{-10} \text{ cm}^2/\text{s}$, assuming (as they did) that the charge transport rates observed in their studies give a measure of the diffusion coefficient of bisulfate ion in PA films. Thus, even with potential errors of several orders of magnitude in these values, it certainly seems reasonable to postulate that proton transport in the composite film will be faster than anion transport in the simple film.

Conclusions

The fabrication of composite films of poly(aniline) using Nafion as a matrix material has been shown to endow the resulting heterogeneous material with several desirable properties. It is especially significant that the pH range of useful behavior is extended, as some of the proposed battery applications for PA (15) would be more feasible if the material were electrochemically well behaved in other than acidic solutions. The increased charging rate at higher pH values of the composite films relative to the simple films is also advantageous in this context. This strategy of forcing protons (or any other rapidly moving ions) to carry charge during switching appears to be quite general in its applicability to the problem of increasing charge transport rates, and can be rationally applied to any composite system, given an understanding of the transport properties of the matrix material.

While the mechanical properties of these composite films have not been studied, it has been observed that the physical ruggedness of the films (e.g. to abrasion or rapid, turbulent solvent flow) is considerably enhanced relative to the simple films. This is especially true for larger values of film thickness, where the simple films become powdery and lack adhesion to the

electrode surface while the composite films adhere tenaciously. This qualitative enhancement in mechanical properties of composite films is not unexpected, and represents a useful additional benefit of the composite structure.

In a general sense, the present study provides another confirmation of a notion about composite structures that has been propounded by many in the literature (4-11), namely that such structures may be used to favorably influence charge transport rates. Perhaps more importantly, it has been shown here that the thermodynamics of the redox process can be influenced by such structures.

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Figure Captions.

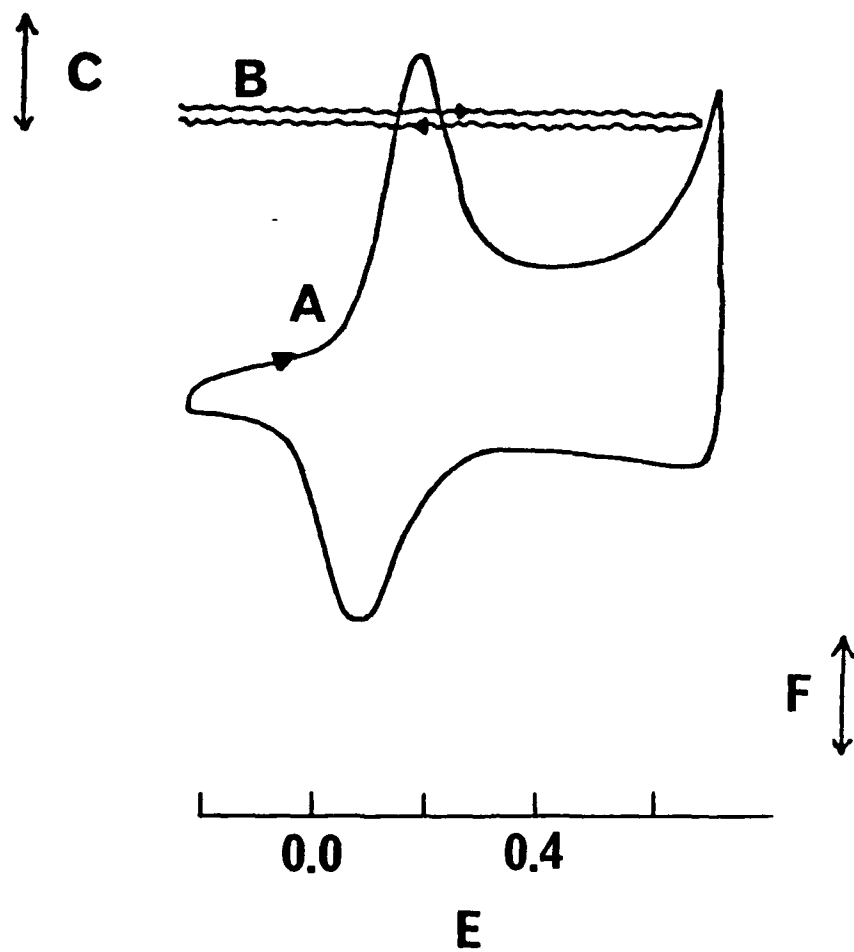
Figure 1. A) CV of growth of PA in Nafion film in solution of 0.1 M aniline, 1.0 M H_2SO_4 . Scan rate - 200 mV/s. C = 20 microamps. B) QCM response obtained simultaneously with CV in (A). F = 10 Hz.

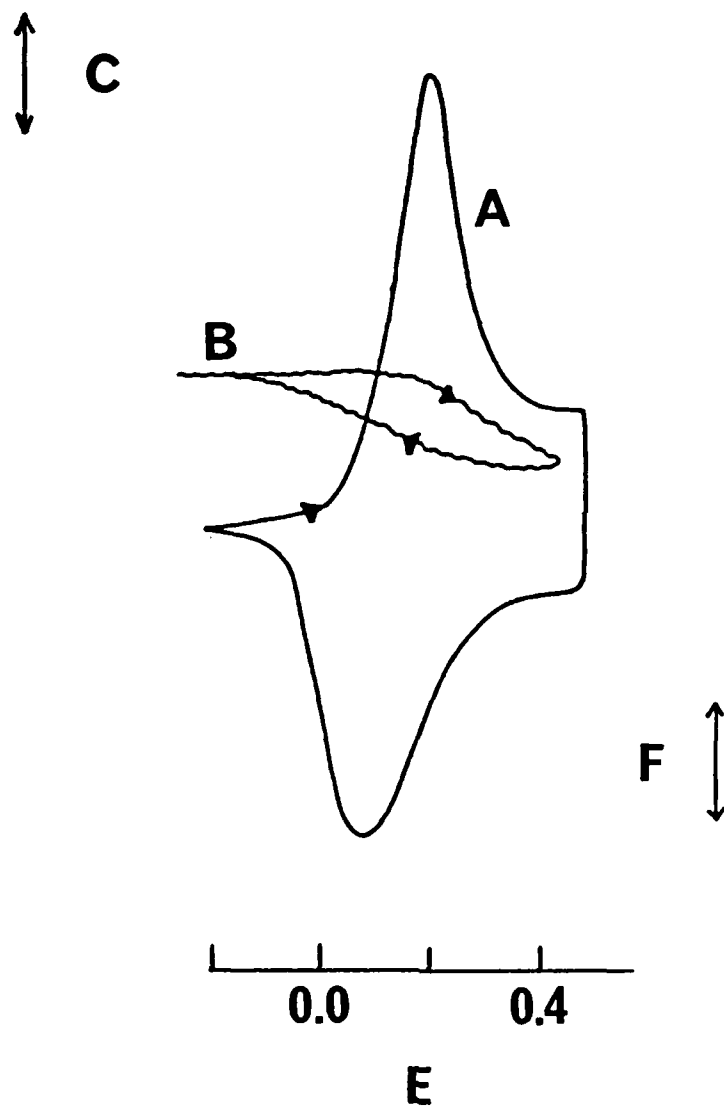
Figure 2. A) CV as in Figure 1A above. All conditions the same, except that the PA thickness is larger. See text for details. C = 200 microamps. B) QCM response as in Figure 1B. F = 40 Hz.

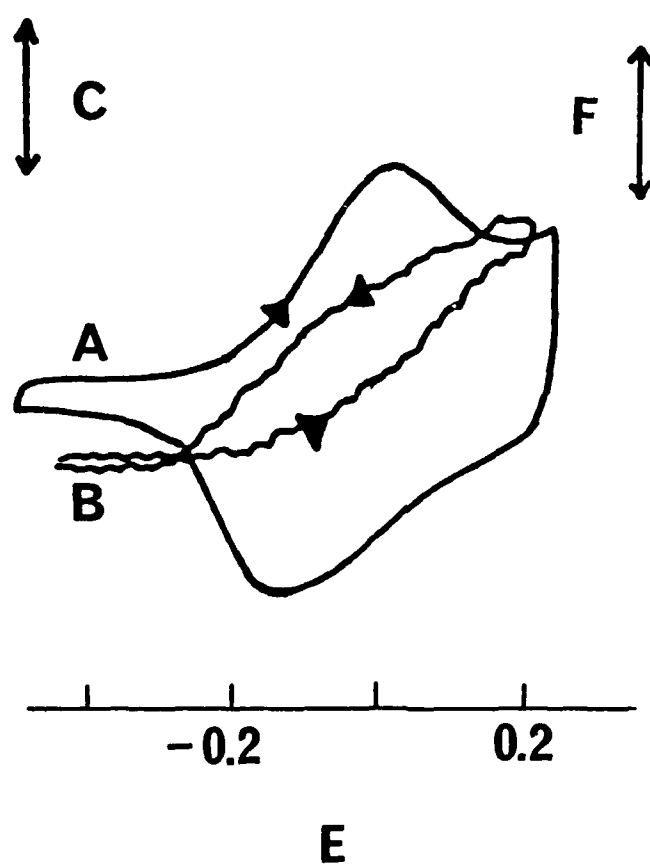
Figure 3. A) CV of PA/Nafion composite film in 0.1 M CsCl. Scan rate - 200 mV/s. C = 20 microamps. B) QCM response. F = 5 Hz.

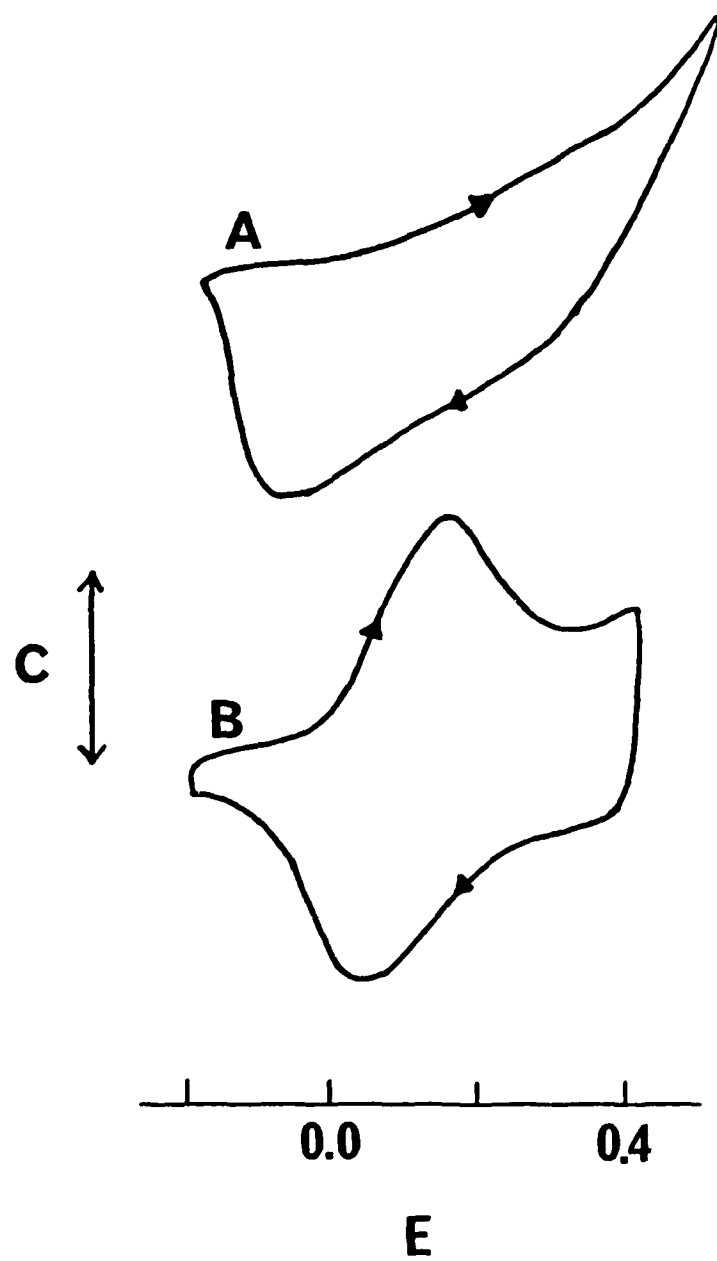
Figure 4. CV in 0.1 M H_2SO_4 with 0.1 M NaOH added to give a pH of 2. Scan rate - 200 mV/s. C = 25 microamps. A) Simple PA film. B) PA/Nafion composite film.

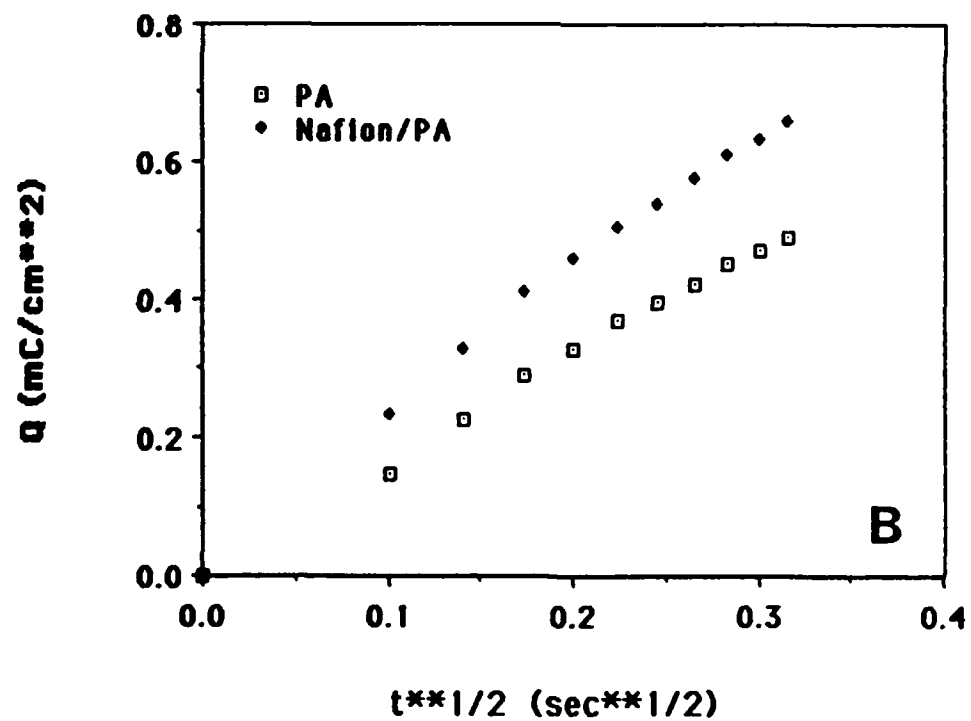
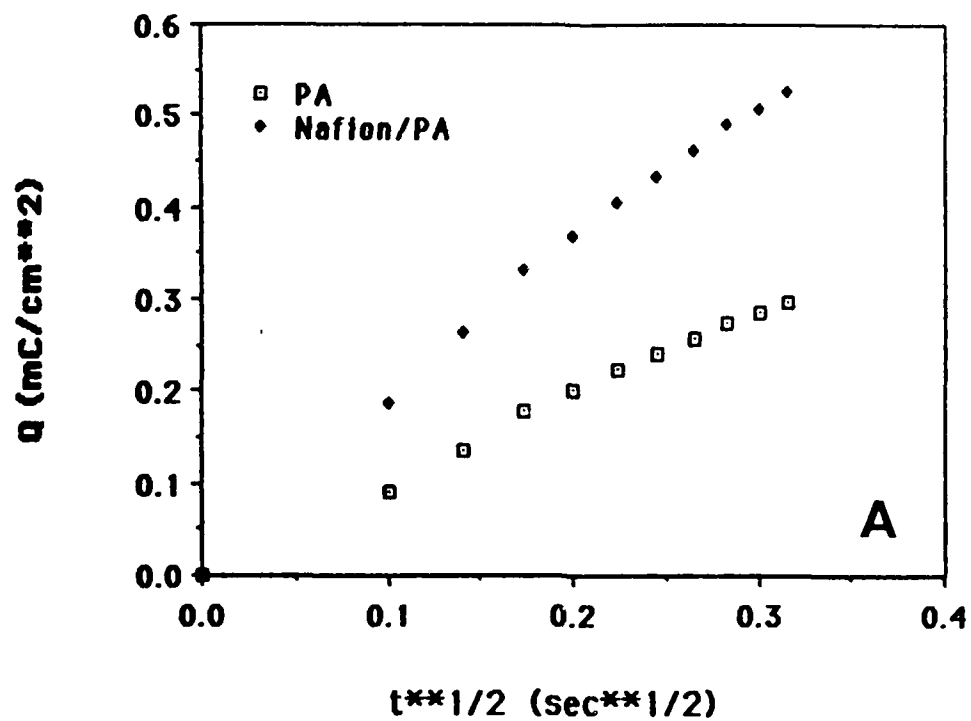
Figure 5. Charge versus $t^{1/2}$ curves for both PA (open symbols) and PA/Nafion composite (closed symbols) films for potential step from -0.2 to 0.5 V. Solutions contained $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ at ionic strength 0.1. A) pH = 4. B) pH = 3.

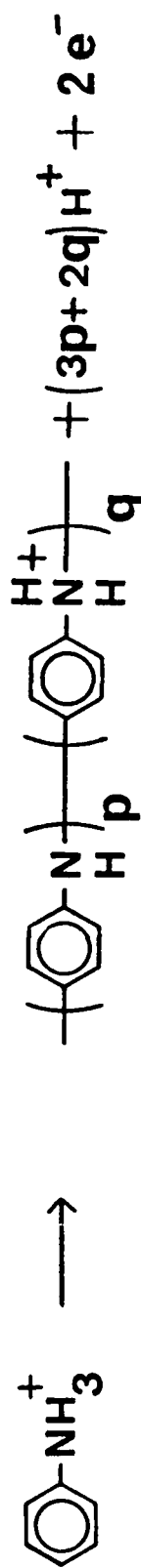












Scheme 1

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